

TRANSMITTAL TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

MAT-7999US

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/601234

INTERNATIONAL APPLICATION NO.
PCT/JP99/06686INTERNATIONAL FILING DATE
30 November 1999 (30.11.99)PRIORITY DATE CLAIMED
02 December 1998 (02.12.98)

TITLE OF INVENTION

NON-AQUEOUS ELECTROLYTE SECONDARY CELL

APPLICANT(S) FOR DO/EO/US

Kenichi MORIGAKI, Kazuya IWAMOTO, Hizuru KOSHINA, Harunari SHIMAMURA and Yoshiaki NITTA

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)). (UNEXECUTED)
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 20 below concern document(s) or information included:

13. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☒ Certificate of Mailing by Express Mail
20. ☐ Other items or information:

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

INTERNATIONAL APPLICATION NO.

ATTORNEY'S DOCKET NUMBER

09/601234

PCT/JP99/06686

MAT-7999US

21. The following fees are submitted:

CALCULATIONS PTO USE ONLY

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

- ☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$970.00
- ☒ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$840.00
- ☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$690.00
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$670.00
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$96.00

ENTER APPROPRIATE BASIC FEE AMOUNT =**\$840.00**Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).**\$0.00**

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total claims	14 - 20 =	0	x \$18.00
Independent claims	2 - 3 =	0	x \$78.00

\$0.00**\$0.00**Multiple Dependent Claims (check if applicable). ☒**\$260.00****TOTAL OF ABOVE CALCULATIONS =****\$1,100.00**Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable). ☐**\$0.00****SUBTOTAL =****\$1,100.00**Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).**\$0.00****TOTAL NATIONAL FEE =****\$1,100.00**Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). ☐**\$0.00****TOTAL FEES ENCLOSED =****\$1,100.00**

Amount to be:

\$

charged

\$

☒ A check in the amount of **\$1,100.00** to cover the above fees is enclosed.☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **18-0350** A duplicate copy of this sheet is enclosed.**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Lawrence E. Ashery
 Ratner & Prestia
 P.O. Box 980
 Valley Forge, PA 19482
 (610) 407-0700

SIGNATURE

Allan Ratner

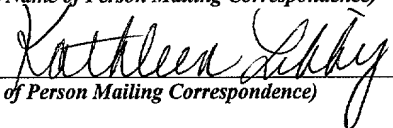
NAME

19,717

REGISTRATION NUMBER

July 31, 2000

DATE

CERTIFICATE OF MAILING BY "EXPRESS MAIL" (37 CFR 1.10) Applicant(s): K. Morigaki et al.			Docket No. MAT-7999US	
Serial No. To Be Assigned	Filing Date Herewith	Examiner	Group Art Unit	
Invention: NON-AQUEOUS ELECTROLYTE SECONDARY CELL				
<p>I hereby certify that the following correspondence:</p> <div style="border: 1px solid black; padding: 10px; margin: 10px 0;"> PCT National Stage Application with PTO-1390 and its enclosures </div> <p style="text-align: center;"><i>(Identify type of correspondence)</i></p> <p>is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 in an envelope addressed to: The Assistant Commissioner for Patents, Washington, D.C. 20231 on</p> <p style="text-align: center;"> <u>July 31, 2000</u> <i>(Date)</i> </p> <div style="text-align: right; margin-top: 20px;"> <p>Kathleen Libby <i>(Typed or Printed Name of Person Mailing Correspondence)</i></p> <p> <i>(Signature of Person Mailing Correspondence)</i></p> <p>EL635062205US <i>("Express Mail" Mailing Label Number)</i></p> </div>				
<p>Note: Each paper must have its own certificate of mailing.</p>				

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: K. Morigaki et al.	: Art Unit:
Serial No.: To Be Assigned	: Examiner:
Filed: Herewith	: Box PCT
FOR: NON-AQUEOUS ELECTROLYTE	:
SECONDARY BATTERY	:

SUPPLEMENTAL PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231
S I R :

Prior to examination, please amend the above application as follows:

IN THE CLAIMS:

Please amend the claims as follows:

- 1 1. (Amended) A non-aqueous electrolyte secondary battery
- 2 comprising;
- 3 a positive electrode and a negative electrode capable of intercalating
- 4 and de-intercalating lithium;
- 5 a non-aqueous electrolyte solution; and
- 6 a solid electrolyte,
- 7 wherein said negative electrode includes a plurality of composite
- 8 particles, each composite particle includes:
- 9 a central portion containing at least one of tin, silicon and zinc; and
- 10 a coating at least partially around said central portion, said coating
- 11 including at least one of a solid solution and an inter-metallic compound
- 12 containing a) at least one of tin, silicon and zinc, and b) at least one element

selected from the group consisting of group 2 elements, transition elements, group 12 elements, group 13 elements and group 14 elements exclusive of carbon;

[contains a composite particle constructed such that at least part of a surface of a nuclear particle containing at least one of tin, silicon and zinc as a constituent element is coated with one of;

a solid solution, and

an inter-metallic compound,

which are composed of an element included in said nuclear particle and at least one element, exclusive of the element included in said nuclear particle, selected from a group of elements in a Periodic Table, comprising group 2 elements, transition elements, group 12 elements, group 13 elements and group 14 elements exclusive of carbon,]

[and] wherein said solid electrolyte is a polymer gel electrolyte.

4. (Amended) The non-aqueous electrolyte secondary battery of one of claim 1 and claim 2 wherein said polymer is one of a polymer and a copolymer including at least one monomer selected from [a] the group [comprising] consisting of acrylonitrile, vinylidene fluoride, hexafluoropropylene, tetrafluoro-ethylene, and perfluoro-alkyl vinyl ether.

5. (Amended) The non-aqueous electrolyte secondary battery of one of claim 1 and claim 2, wherein said polymer is a polyester polymer whose [main] structure is one of polyester and a derivative of the same.

8. (Amended) A non-aqueous electrolyte secondary battery comprising;

a positive electrode and a negative electrode capable of intercalating and de-intercalating lithium;

a non-aqueous electrolyte solution; and

a solid electrolyte,

7 wherein said negative electrode includes a plurality of composite
8 particles, each composite particle includes:

9 a central portion containing at least one of tin, silicon and zinc; and

10 a coating at least partially around said central portion, said coating

11 including at least one of a solid solution and an inter-metallic compound

12 containing a) at least one of tin, silicon and zinc, and b) at least one element

13 selected from the group consisting of group 2 elements, transition elements, group

14 12 elements, group 13 elements and group 14 elements exclusive of carbon;

15 [contains a composite particle constructed such that at least part of a
16 surface of a nuclear particle containing at least one of tin, silicon and zinc as a
17 constituent element is coated with one of;

18 a solid solution, and

19 an inter-metallic compound,

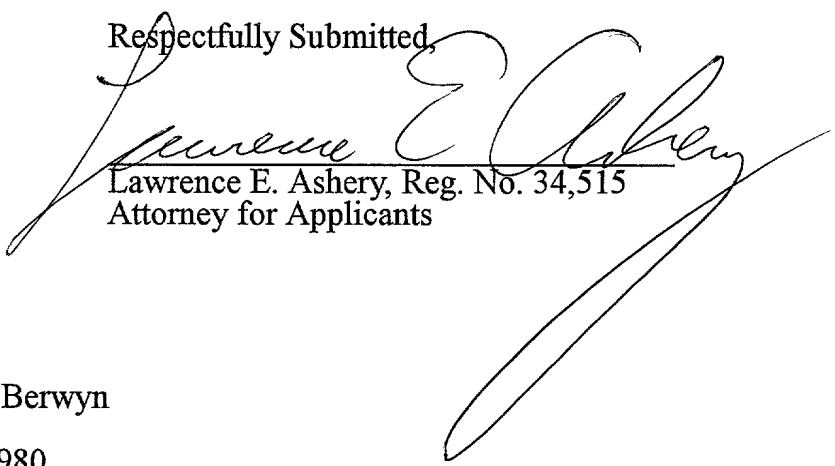
20 which are composed of elements included in said nuclear particle
21 and at least one element, exclusive of the element included in said nuclear particle,
22 selected from a group of elements in a Periodic Table, comprising group 2
23 elements, transition elements, group 12 elements, group 13 elements and group 14
24 elements exclusive of carbon,]

25 [and] wherein said solid electrolyte is a lithium ion conductive glass-
26 type solid electrolyte.

IN THE ABSTRACT:

Please delete the Abstract in its entirety and substitute therefor the Abstract enclosed on the attached separate sheet.

Respectfully Submitted,


Lawrence E. Ashery, Reg. No. 34,515
Attorney for Applicants

LEA/dlm/lm

Dated: October 30, 2000


Suite 301, One Westlakes, Berwyn
P.O. Box 980
Valley Forge, PA 19482-0980
(610) 407-0700

The Assistant Commissioner for Patents is hereby authorized to charge payment to Deposit Account No. **18-0350** of any fees associated with this communication.

EXPRESS MAIL Mailing Label Number: EL629503836US

Date of Deposit: October 30, 2000

I hereby certify that this paper and fee are being deposited, under 37 C.F.R. § 1.10 and with sufficient postage, using the "Express Mail Post Office to Addressee" service of the United States Postal Service on the date indicated above and that the deposit is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.


Kathleen Libby
Bobbie Duzham

ABSTRACT

A negative electrode of a non-aqueous electrolyte secondary battery contains, as main a component, composite particles constructed in such a manner that at least part of the surface of nuclear particles comprising at least one of tin, silicon and zinc as a constituent element, is coated with a solid solution or an inter-metallic compound composed of elements included in the nuclear particle and at least one element, exclusive of the element included in said nuclear particle, selected from a group of elements in a Periodic Table, comprising group 2 elements, transition elements, group 12 elements, group 13 elements and group 14 elements exclusive of carbon. The batteries of the present invention include non-aqueous electrolytic solution and solid electrolytes comprising polymer gel electrolytes. The construction of the present invention provides a non-aqueous electrolytic secondary battery with which a possibility of the generation of gas is extremely low when stored at high temperatures. It also provides a battery having higher capacity, and superior cycle properties, high-rate charge/discharge properties.

09/601234

533 Rec'd PCT/PTO 31 JUL 2000

MAT-7999US

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: K. Morigaki et al.	: Art Unit:
Serial No.: To Be Assigned	: Examiner:
Filed: Herewith	:
FOR: NON-AQUEOUS ELECTROLYTE	:
SECONDARY CELL	:

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents

Washington, D.C. 20231

S I R :

Prior to examination, please amend the above application as follows:

IN THE TITLE:

Please delete the title in this entirety and substitute therefore
--NON-AQUEOUS ELECTROLYTE SECONDARY BATTERY--.

IN THE DRAWINGS:

Please delete sheet "3/3", also labeled as "Reference numerals".

IN THE SPECIFICATION:

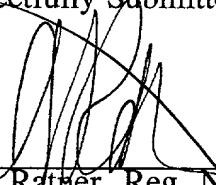
After the title and before the first paragraph, please insert --THIS APPLICATION IS A U.S. NATIONAL PHASE APPLICATION OF PCT INTERNATIONAL APPLICATION PCT/JP99/06686--.

On page 4, line 8, the word "precious" should read --noble--.

On page 4, line 19, the word "precious" should read --noble--.

On page 4, line 26, the word "precious" should read --noble--.

Respectfully Submitted,



Allan Rather, Reg. No. 19,717
Attorney for Applicants

AR/dlm
Suite 301, One Westlakes, Berwyn
P.O. Box 980
Valley Forge, PA 19482-0980
(610) 407-0700

The Assistant Commissioner for Patents is
hereby authorized to charge payment to Deposit
Account No. **18-0350** of any fees associated
with this communication.

EXPRESS MAIL Mailing Label Number: EL635062205US

Date of Deposit: July 31, 2000

I hereby certify that this paper and fee are being deposited, under 37 C.F.R. § 1.10 and with sufficient postage,
using the "Express Mail Post Office to Addressee" service of the United States Postal Service on the date
indicated above and that the deposit is addressed to the Assistant Commissioner for Patents, Washington,
D.C. 20231.



Kathleen Libby

Non-aqueous electrolyte secondary battery

Field of the Invention

5 The present invention relates to a non-aqueous electrolyte secondary battery (hereinafter, battery), and especially relates to batteries of which electrochemical properties such as the charge/discharge capacity and charge/discharge cycle life have been enhanced by improvements in negative electrode materials and non-aqueous electrolytes.

Background of the Invention

10 In recent years, lithium secondary batteries with non-aqueous electrolytes, which are used in such fields as mobile communications devices including portable information terminals and portable electronic devices, main power sources of portable electronic devices, domestic portable electricity storing devices, motor cycles using an electric motor as a driving source, electric cars and hybrid electric cars, have characteristics of a high electromotive force and a high energy density.

20 The lithium ion secondary batteries which contain an organic electrolytic solution, and use carbon materials as negative electrode active materials and lithium-containing composite oxides as positive electrode active materials, have higher voltage and energy density, and superior low temperature properties compared with secondary batteries using aqueous solutions. As these
25 lithium ion batteries do not use lithium metal for the negative electrode, they are superior in terms of cycle stability and safety, thus are now being commercialized rapidly. Lithium polymer batteries using macromolecular (polymer) gel electrolytes which contain an organic electrolytic solution, have been also under development as a new thin and light batteries.

30 As for polymer electrolyte batteries, various researches have been conducted on the subject since Armand et al. disclosed a polymer electrolyte

battery comprising polyethylene oxides and electrolytic salts (Second International Meeting on Solid Electrolytes, Extended Abstracts, p20-22, 1978, United States Patent No. 4,303,748). Although various polymer electrolytic materials have been mentioned, for example, in *the conductive polymer* edited by Naoya Ogata, Kodansha, 1990, and *Polymer Electrolyte Reviews, Vol.1 and 2*, Elsevier, London (1987, 1989), ionic conductivity of these polymer electrolytic materials at room temperature is only about 10^{-4} - 10^{-5} S/cm.

As another method to improve ionic conductivity, different types of electrolytes which can easily achieve the ionic conductivity of 10^{-3} S/cm have been disclosed, for example, in J. Electrochem. Soc., 137, 1657 (1990), United States Patent No. 5085952, United States Patent No. 5223353 and United States Patent No. 5275750. These electrolytes are called polymer gel electrolyte in which solvents of organic electrolytic solutions are added to polymers as plasticizers. Polymer batteries using these polymer gel electrolytes are expected to achieve the same performance as lithium ion batteries by improving ionic conductivity. However, in respect of capacity, both positive electrode and negative electrodes of these polymer batteries need to be made of composite materials containing polymers as well. Thus, the mass (density) of active materials in the casing of the battery is reduced. Therefore, when the same materials are used for both positive and negative electrodes, energy density of the lithium polymer secondary batteries becomes lower than that of the lithium ion batteries.

When a high-capacity lithium metal is used as a negative electrode material, dendritic deposits are formed on the negative electrode during charging. Over repeated charging and discharging, these dendritic deposits penetrate through separators and polymer gel electrolytes to the positive electrode side, causing an internal short circuit. The deposited dendrites have a large specific surface area, thus their reaction activity is high. Therefore, they react with plasticizers (solvents) of the polymer gel electrolytes, lowering charge/discharge efficiency. Due to these reasons, the lithium secondary batteries using lithium metal as a negative electrode material have a low reliability and a short cycle life.

To suppress the formation of such dendrites, it has been disclosed that lithium alloys such as lithium - aluminum alloy and a wood's alloy are used instead of lithium metal. Metals capable of forming alloys with lithium and alloys containing at least one such metal can be used as a negative electrode material with a relatively high electrochemical capacity in the initial charge/discharge cycle. However, by repeatedly alloying with and de-intercalating lithium, they may undergo a phase change even when the crystal structure of the original skeletal alloy is maintained, or sometimes, the crystal structure of the skeletal alloy of elements changes. In this case, particles of the metal or alloy which are host materials of the lithium, an active material, swell and shrink. As the charge/discharge cycle proceeds, crystal grains are stressed and cracked, thus particles are pulverized and come off from the electrode plate. As the crystal grains are pulverized, resistance and contact resistance of the grain boundaries increase. As a result, resistance polarization during charging and discharging increases. Thus, when charging is conducted at a controlled voltage level, charging depth becomes shallow, limiting the amount of electricity charged in the battery. On the other hand, during discharging, the voltage drop occurs by the resistance polarization, reaching the discharge-termination voltage early. Thus, superior charge/discharge capacity and cycle properties can not be expected.

If currently used solvents such as ethylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, propylene carbonate, gamma-butyro lactone, and gamma-valero lactone are used in a system in which lithium metal or a lithium alloy is used in a negative electrode, the electrolyte may decompose and gas may be produced when the battery is fully charged and stored at high temperatures. Moreover, if the battery is repeatedly charged and discharged, parallel to the charge/discharge reaction of the negative electrode, the electrolyte is gasified, lowering the charge/discharge efficiency, resulting in decreased cycle properties.

Nowadays, lithium secondary batteries which use, as a negative electrode material, carbon materials capable of intercalating and de-intercalating

lithium ions, are commercially available. In general, lithium metal does not deposit on carbon negative electrodes. Thus, short circuits are not caused by dendrite. However, the theoretical capacity of graphite which is one of currently used carbon materials is 372 mAh/g, only one tenth of that of pure Li metal.

If graphite-group carbon materials are used as a negative electrode material, and propylene carbonate is adopted for an electrolytic solution, the electrolytic solution is decomposed at potentials more precious than that of lithium metal. Consequently, lithium ions are not intercalated between layers of graphite, and the battery does not function. Considering these points, currently commercialized lithium secondary batteries with the graphite-group used for negative electrode materials frequently use electrolytic solution containing ethylene carbonate. However, the melting point of ethylene carbonate is 37°C higher than room temperature. Therefore, at low temperatures, ionic conductivity of the electrolytic solution for lithium ions plummets, lowering charge/discharge priorities.

When inorganic compound materials such as TiS_2 are used as a negative electrode active material, intercalation and de-intercalation of lithium occur at sufficiently more precious potentials compared with lithium metal and lithium alloys. Thus, even when the negative electrode active materials come in contact with the electrolytic solution, reductive decomposition does not occur. Moreover, even when propylene carbonate is used for the electrolytic solution, intercalation and de-intercalation are not impeded by decomposition as it is the case with the graphite materials, therefore, a wider range of electrolytic solutions are applicable. However, potentials of the negative electrode using the foregoing inorganic compound materials is precious, causing voltage of the battery to inevitably become low. This is a disadvantage of achieving higher energy density.

Regarding the supporting electrolytes, the thermal stability of LiClO_4 , LiBF_4 , and LiPF_6 needs to be improved. Furthermore, above fluorine-containing inorganic anion salts react with minute amounts of water contained in

an electrolytic solution and decompose.

To form a totally solid-state battery by using, as non-aqueous electrolytes and lithium ion conductor glass-type solid electrolytes, solid electrolytes in powder form need to be mixed in the electrode to secure and maintain ionic conductivity in the electrode. However, electrodes constructed in the manner mentioned above are brittle, and incapable of absorbing expansion and shrinkage of the electrode materials that occur during charging and discharging. In other words, the electrode itself merely expands as it lacks resilience. Therefore, once it expands, it does not shrink. Therefore, some particles fail to contact with one another properly, increasing the number of particles in the electrode material which can not contribute to charging and discharging. As a result, the properties of the battery are lowered.

Other known negative electrode materials include pure metallic materials and pure non-metallic materials which form compounds with lithium. For example, composition formulae of compounds of tin (Sn), silicon (Si) and zinc (Zn) with the maximum amount of lithium are respectively $\text{Li}_{22}\text{Sn}_5$, $\text{Li}_{22}\text{Si}_5$, and LiZn . Within the range of these composition formulae, metallic lithium does not normally deposit. Thus, an internal short circuit is not caused by dendrite. Furthermore, the electrochemical capacities between these compounds and each element mentioned above are respectively 993 mAh/g, 4199 mAh/g and 410 mAh/g; all are larger than the theoretical capacity of graphite.

As other compound negative electrode materials, the Japanese Patent Laid-Open Publication No. H07-240201 discloses a non-metallic silicide comprising transition elements. The Japanese Patent Laid-Open Publication No. H09-63651 discloses negative electrode materials which are made of inter-metallic compounds comprising at least one of group 4B elements, P and Sb, and have a crystal structure of one of the CaF_2 type, the ZnS type and the AlLiSi type.

However, the foregoing high-capacity negative electrode materials have the following problems.

Negative electrode materials of pure metallic materials and pure non-metallic materials which form compounds with lithium have inferior charge/discharge cycle properties compared with carbon negative electrode materials. The reason for this is assumed to be the destruction of the negative electrode materials caused by their volume expansion and shrinkage.

On the other hand, as negative electrode materials with an improved cycle life property unlike the foregoing pure materials, the Japanese Patent Laid-Open Publication No. H07-240201 and the Japanese Patent Laid-Open Publication No. H09-63651 respectively disclose non-metallic silisides composed of transition elements and inter-metallic compounds composed of at least one of group 4B elements, P and Sb, and which have a crystal structure of one of the CaF_2 type, the ZnS type and the AlLiSi type.

Batteries using the negative electrode materials of the non-metallic silisides composed of transition elements are disclosed in the Japanese Patent Laid-Open Publication No. H07-240201. The capacities of the embodiments of the invention and a comparative example at the first cycle, the fiftieth cycle and the hundredth cycle suggest that the batteries of the invention have improved charge/discharge cycle properties compared with lithium metal negative electrode materials. However, when compared with a natural graphite negative electrode material, the increase in the capacity of the battery is only about 12%.

The materials disclosed in the Japanese Patent Laid-Open Publication No. H09-63651 have a better charge/discharge cycle property than a Li-Pb alloy negative electrode material according to an embodiment and a comparative example. The materials also have a larger capacity compared with a graphite negative electrode material. However, the discharge capacity decreases significantly up to the 10-20th charge/discharge cycles. Even when Mg_2Sn , which is considered to be better than any of the other materials, is used, the discharge capacity decreases to approximately 70% of the initial capacity after about the 20th cycle. Thus, their charge/discharge properties are inferior.

Summary of the Invention

The present invention relates to a non-aqueous electrolyte secondary battery comprising:

- a positive electrode and a negative electrode capable of intercalating and de-intercalating lithium, and
- as non-aqueous electrolytes,
- lithium ion conductive glass-type solid electrolytes, or
- polymer gel electrolytes using a polymer comprising at least one of;
 - polyalkylene oxides or their derivatives, specific polymers which containing fluorine, polyacrylonitrile, polyester, and copolymers of methacrylate and ethylene oxides,

The negative electrode is characterized by its main material which uses composite particles constructed in such a manner that at least part of the surrounding surface of nuclear particles containing at least one of tin, silicon and zinc as a constituent element , is coated with a solid solution or an inter-metallic compound composed of an element included in the nuclear particles and at least one element (exclusive of the elements included in the nuclear particles) selected from a group comprising group 2 elements, transition elements, group 13 elements and group 14 elements (exclusive of carbon) of the Periodic Table. With the foregoing construction, an internal short circuit between the positive electrode and the negative electrode caused by the expansion of the negative electrode materials can be restricted, thereby achieving high capacity, high energy density batteries with superior charge/discharge cycle properties.

The lithium ion conductive glass-type solid electrolytes of the present invention includes ; at least lithium sulfide as a first component; one or more compounds selected from silicon sulfides, phosphor sulfides and boron sulfides as a second component; and one or more compounds selected from lithium phosphate, lithium sulfate, lithium borate, lithium silicate as a third component. The lithium ion conductive glass-type solid electrolytes is synthesized with above three components.

The construction of the present invention achieves novel non-aqueous

electrolytic secondary batteries which rarely suffer generation of gas when stored at high temperatures. Moreover, even when the batteries are repeatedly charged and discharged, charge/discharge efficiency of their negative electrode does not decrease. The batteries can be used in a wide range of temperatures.

5 Furthermore, the batteries enjoy high energy density and a lower reduction rate of discharge capacity when used repeatedly as well as high charge/discharge properties.

Brief Description of the Drawings

10 Fig. 1 shows a cross-section of a flat type non-aqueous electrolyte battery of the present invention.

Fig. 2 shows vertical cross section of a cylindrical battery of the present invention.

Detailed Description of Preferred Embodiments

As a negative electrode material used in the present invention, composite particles whose nuclear particles composed of solid phase A are coated with solid phase B over the whole surface or part of the surface, are used.

20 The solid phase A contains at least one of tin, silicon and zinc as a constituent element. The solid phase B is composed of a solid solution or inter-metallic compounds composed of at least one of tin, silicon and zinc and at least one element (exclusive of the foregoing constituent elements) selected from a group comprising group 2 elements, transition elements, group 12 elements, group 13 elements and group 14 elements (exclusive of carbon) of the Periodic Table.

25 Hereinafter, the foregoing negative electrode materials are called "composite particles". When the composite particles are used as a negative electrode material, the solid phase B helps to suppress expansion and shrinkage of the solid phase A caused by charging and discharging, thereby achieving a negative

30 electrode material with superior charge/discharge cycle properties.

It can be considered that the solid phase A of the negative electrode material of the present invention mainly contributes to a higher charge/discharge capacity since it contains at least one of Sn, Si and Zn. The solid phase B which coats the whole or part of the surrounding surface of the nuclear particles comprising the solid phase A, contributes to improvement of the charge/discharge cycle properties. The amount of lithium contained in the solid phase B is normally less than that contained in metal, a solid solution or an inter-metallic compound.

In other words, the negative electrode material used in the present invention is constructed such that particles containing at least one of high-capacity Sn, Si and Zn as a constituent element, are coated with the solid solution or the inter-metallic compound, which are resistant to pulverization. The solid solution or the inter-metallic compounds in the coating layer prevent significant changes in crystal structure, namely changes in volume of the nuclear particles caused by electrochemical intercalating and de-intercalating of lithium. In this manner, pulverization of nuclear particles is restricted.

The following is a manufacturing method of composite particles used for the negative electrode materials.

In one manufacturing method of the composite materials, a fused mixture of elements contained in the composite particles at a predetermined composition ratio is quenched and solidified by dry-spraying, wet-spraying, roll-quenching or turning-electrode method. The solidified material is heat treated at the temperature lower than the solid line temperature of a solid solution or inter-metallic compounds. The solid line temperature is determined by the composition ratio. The process of quenching and solidifying of the fused mixture allows the solid phase A to deposit as a nucleus of a particle, and at the same time, allows the solid phase B, which coats part of or the whole surface of the solid phase A, to deposit. The heat treatment following the foregoing process enhances evenness of the solid phase A and the solid phase B. Even when the heat treatment is not conducted, composite particles suitable for the present invention can be obtained. Apart from the quenching method

mentioned above, other methods are applicable providing they can cool the fused mixture rapidly and adequately.

In another manufacturing method, a layer of deposits comprising essential elements in forming solid phase B is formed on the surface of the powder of the solid phase A. The layer is treated at temperatures lower than the solid line temperature. This heat treatment allows constituent elements within the solid phase A to disperse throughout the deposit layer to form the solid phase B as a coating layer. The deposit layer can be formed by plating or by a mechanical alloying method. In the case of the mechanical alloying method, the heat treatment is not necessary. Other methods can also be used on the condition that they can form the surface deposit layer.

As a conductive material for the negative electrode, any electronic conduction materials can be used. Examples of such materials include graphite materials including natural graphite (scale-like graphite), synthetic graphite and expanding graphite; carbon blacks such as acetylene black, Ketzen black (registered trademark of highly structured furnace black), channel black, furnace black, lamp black and thermal black; conductive fibers such as carbon fibers and metallic fibers; metal powders such as copper and nickel; and organic conductive materials such as polyphenylene derivatives. These materials can be used independently or in combination. Among these conductive materials, synthetic graphite, acetylene black and carbon fibers are especially favorable.

The total amount of the conductive materials is not specifically defined, however, 1-50wt%, especially 1-30% of the negative electrode materials is desirable. As negative electrode materials (composite particles) of the present invention are themselves conductive, even if conductive materials are not added, the battery can still actually function. Therefore, the battery has more room available to contain composite particles.

Binders for the negative electrode can be either thermoplastic resin or thermosetting resin. Desirable binders for the present invention includes the following materials; polyethylene, polypropylene, poly-tetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), styrene - butadiene rubber, a

tetrafluoroethylene - hexafluoropropylene copolymer (FEP), a
 tetrafluoroethylene - perfluoroalkyl vinyl ether copolymer (PFA), a vinyliden
 fluoride - hexafluoropropylene copolymer, a vinyliden fluoride -
 chlorotrifluoroethylene copolymer, a ethylene - tetrafluoroethylene copolymer
 5 (ETFE), poly chlorotrifluoroethylene (PCTFE), a vinyliden fluoride -
 pentafluoropropylene copolymer, a propylene - tetrafluoroethylene copolymer, a
 ethylene - chlorotrifluoroethylene copolymer (ECTFE), a vinyliden fluoride -
 hexafluoropropylene - tetrafluoroethylene copolymer, a vinyliden fluoride
 perfluoromethyl vinyl ether - tetrafluoroethylene copolymer, an ethylene - acrylic
 10 acid copolymer or its Na⁺ ion crosslinking body, an ethylene - methacrylic acid
 copolymer or its Na⁺ ion crosslinking body, a methyl acrylate copolymer or its
 Na⁺ ion crosslinking body, and an ethylene methyl methacrylate copolymer or its
 Na⁺ ion crosslinking body. Favorable materials among these materials are
 styrene butadiene rubber , polyvinylidene fluoride, an ethylene - acrylic acid
 15 copolymer or its Na⁺ ion crosslinking body, an ethylene - methacrylic acid
 copolymer or its Na⁺ ion crosslinking body, a methyl acrylate copolymer or its
 Na⁺ ion crosslinking body, and an ethylene methyl methacrylate copolymer or its
 Na⁺ ion crosslinking body.

As a current collector for the negative electrode, any electronic
 20 conductor can be used on the condition that it does not chemically change in the
 battery. For example, stainless steel, nickel, copper, titanium, carbon,
 conductive resin, as well as copper and stainless steel whose surfaces are coated
 with carbon, nickel or titanium can be used. Especially favorable materials are
 copper and copper alloys. Surfaces of these materials can be oxidized. It is
 25 desirable to treat the surface of the current collector to make it uneven. Usable
 forms of the foregoing materials as the current collector include a foil, a film, a
 sheet, a mesh sheet, a punched sheet a lath form, a porous form, a foamed form
 and a fibrous form. The thickness is not specifically defined however, normally
 those of 1-500 μ m in thickness are used.

30 As positive electrode active materials, lithium containing compounds
 or compounds not containing lithium can be used. Such compounds include

Li_xCoO₂, Li_xNiO₂, Li_xMnO₂, Li_xCo_yNi_{1-y}O₂, Li_xCo_yM_{1-y}O₂, Li_xNi_{1-y}M_yO₂,
 Li_xMn₂O₄, Li_xMn_{2-y}M_yO₄ (M is at least one of Na, Mg, Sc, Y, Mn, Fe, Co, Ni, Cu,
 Zn, Al, Cr, Pb, Sb and B, and x=0-1, Y=0-0.9, z=2.0-2.3). The value of x is the
 value before charging and discharging, thus it changes along with charging and
 5 discharging. Other usable positive electrode materials include transition metal
 chalcogenides, a vanadium oxide and its lithium compounds, a niobium oxide
 and its lithium compounds, a conjugate polymer using organic conductive
 materials, and shevrit phase compounds. It is also possible to use a plurality of
 different positive electrode materials in a combined form. The average diameter
 10 of particles of the positive electrode active materials is not specifically defined,
 however, desirably it is 1-30 μ m.

Conductive materials for the positive electrode can be any electronic
 conductive material on the condition that it does not chemically change within
 the range of charge and discharge electric potentials of the positive electrode
 15 materials in use. Examples of such materials include graphite materials
 including natural graphite (scale-like graphite) and synthetic graphite; carbon
 black materials such as acetylene black, Ketjen black, channel black, furnace
 black, lamp black and thermal black; conductive fibers such as carbon fibers and
 metallic fibers; metal powders such as fluorinated carbon and aluminum;
 20 conductive whiskers such as a zinc oxide and potassium titanate, conductive
 metal oxides such as a titanium oxide, and organic conductive materials such as
 polyphenylene derivatives. These materials can be used independently or in
 combination. Among these conductive materials, synthetic graphite and
 acetylene black are especially favorable. The total amount of the conductive
 25 materials to be added is not specifically defined, however, 1-50wt%, especially
 1-30% of the positive electrode materials is desirable. In the case of carbon and
 graphite, 2-15 wt% is especially favorable.

Binders for the positive electrode can be either thermoplastic resin or
 thermosetting resin. The binders for the negative electrode mentioned earlier
 30 can be used effectively, however, PVDF and PTFE are more preferable.

Current collectors for the positive electrode of the present invention

can be any electronic conduction materials on the condition that it does not chemically change within the range of charge and discharge electric potentials of the positive electrode materials in use. For example, the current collectors for the negative electrode mentioned earlier can be used preferably. The thickness of the current collectors is not specifically defined, however, those of 1-500 μ m in thickness are used.

As electrode mixtures for the positive electrode and the negative electrode plates, conductive materials, binders, fillers, dispersants, ionic conductors, pressure enhancers, and other additives can be used. Any fiber materials which do not change chemically in the battery can be used as fillers. In general, fibers made of olefin polymers such as polypropylene and polyethylene, and fibers made of glass and carbon are used as fillers. The amount of the filler to be added is not specifically defined however, it is desirably 0-30wt% of the electrode binders.

As for the construction of the positive electrode and the negative electrode, it is favorable that at least the surfaces of the negative electrode and the positive electrode where the electrode mixtures are coated are facing each other.

The following is a detailed description of the materials used in the batteries of the present invention.

The positive electrode and the negative electrode of the battery of the present invention are constructed such that a current collector is coated with a mixture layer which includes the positive electrode active materials and the negative electrode materials capable of electrochemically and reversibly intercalating and de-intercalating lithium ions as main constituents , and conductive materials as well as binders.

(Manufacture of the composite particles)

In Table 1, components (pure elements, inter-metallic compounds, solid solution) of the solid phase A and the solid phase B of the composite particles used in the preferred embodiments of the present invention, composition

ratios of elements, fusing temperatures, and solid phase line temperatures are shown. Commercially available highly pure reagents are used as ingredients for each element.

To obtain solid materials, powder or a block of each element contained
 5 in the composite particles is put into a fusing vessel in the composition ratio shown in Table 1, and fused at the temperature also shown in Table 1. The fused mixture is quenched by the roll-quenching method and solidified to form a solid material which is then heat treated at temperatures of 10°C-50°C lower than the solid phase line temperatures shown in Table 1, in an inert atmosphere for 20
 10 hours. After being heat treated, the material is ground with a ball mill, and classified using a sieve to prepare composite particles of 45 μ m or less. An electron microscope observation confirmed, part of or the whole surface of the solid phase A are covered with the solid phase B.

Regarding constituent elements of the negative electrode materials,
 15 when the solid phase A is Sn, Mg selected from group 2 elements, Fe and Mo from transition elements, Zn and Cd from group 12 elements, In from group 13 elements and Pb from group 14 elements are used. However, similar results are obtained with other elements selected from each group. The composition ratio of the constituent elements of the negative electrode material is not specifically
 20 defined, on the condition that two phases are created and one of which (solid phase A) is mainly composed of Sn, and partly or entirely covered with the other phase (solid phase B). The solid phase A can be composed not only of Sn but also traces of other elements such as O, C, N, S, Ca, Mg, Al, Fe, W, V, Ti, Cu, Cr, Co, and P.

25 When the solid phase A is Si, Mg selected from group 2 elements, Co and Ni from transition elements, Zn from group 12 elements, Al from group 13 elements and Sn from group 14 elements are used. However, similar results are obtained with other elements selected from each group. Similarly, when the solid phase A is Zn, Mg from group 2 elements, Cu and V from transition
 30 elements, Cd from group 12 elements, Al from group 13 elements and Ge from group 14 elements are used. However, similar results are obtained with other

elements selected from each group. The composition ratio of the constituent elements of the negative electrode material is not specifically defined, on the condition that two phases are created and one of which (solid phase A) is mainly composed of Si and Zn, and partly or entirely covered with the other phase (solid phase B). The solid phase A can be composed not only of Si and Zn but also traces of elements such as O, C, N, S, Ca, Mg, Al, Fe, W, V, Ti, Cu, Cr, Co, and P.

(negative electrode plate)

To prepare the negative electrode plate 6, 20wt% of carbon powder and 5wt% of PVDF are mixed with 75wt% of the composite particles synthesized under the foregoing conditions. The mixture is dispersed in dehydrated N-methyl pyrrolidone to form a slurry. The slurry is coated onto a negative electrode current collector comprising copper foil, dried and rolled under pressure. Instead of PVDF, polymers comprising a polymer gel electrolyte are used as well.

(positive electrode plate)

To prepare the positive electrode plate 5, 10wt% of carbon powder and 5wt% of PVDF are mixed with 85wt% of lithium cobaltate powder. The mixture is dispersed in dehydrated N-methyl pyrrolidinone to form a slurry. The slurry is coated onto a positive electrode current collector comprising copper foil, and dried and rolled under pressure. In stead of PVDF, polymers composing a polymer gel electrolyte are used as well.

(polymer gel electrolyte)

As a polymer of the polymer gel electrolyte, polymers whose main structure are alkylene oxides or their derivatives such as polyethylene oxides and polypropylene oxides are used. Alkylene oxides have comparatively low melting points as polymer materials, and , lithium salts can largely dissolve into them. As such, they are very easy to handle. Although their ionic conductivity is low, this problem can be solved by using organic solvents as a plasticizer.

Other polymers that can be used as a polymer gel electrolyte include

copolymers of two or three compounds selected from a group comprising vinylidene fluoride, hexafluoro propylene, tetrafluoro ethylene, and perfluoro-alkyl vinyl ether. Copolymers of vinylidene fluoride and hexafluoro propylene are especially favorable. These copolymers are chemically stable and can be thermally welded. With these copolymers, porous film can be produced in the following steps. The copolymers are dissolved into solvents such as tetrahydrofuran (THF) and acetone along with a plasticizer such as phthalic acid ester. The solvent is cast and dried to obtain a film. The plasticizer is then removed by using solvents such as ether to obtain a porous film. If an electrolytic solution is injected into this porous film, a gel electrolyte can be obtained. Thus, after forming an integrated construction of an electrode, an electrolytic solution can be injected to produce gel electrolytes.

Other polymers used for the polymer gel electrolytes include polyacrylonitrile or polyacrylonitrile derivative polymers using polyacrylonitrile as a main component and copolymerized with methyl acrylate, vinyl pyrrolidone or vinyl acetate. These polymers can be used as polymer alloys with fluorocarbon resins, polyolefin resins, polyether resins and the like. Polyacrylonitrile polymers can be used for a wide range of purposes. They can be dissolved into solvents such as dimethyl formamide, or can be mixed with an organic electrolytic solution and heated and dissolved, these solutions can be then cast to produce a film. Furthermore, a gel film can be formed by soaking a non-woven porous material in the foregoing solution, heating it and then cooling it. The gel film formed in this manner is fire retardant, and can be handled with ease.

Other polymers used for the polymer gel electrolyte include polyester polymers using polyethylene terephthalate, polybutylene terephthalate or their derivatives used as a main component and copolymerized with ethyl methacrylate, styrene or vinyl acetate. These polyester polymers can also be used as polymer alloys with fluorocarbon resins, polyolefin resins, poly ether resins and the like. Polyester polymers are widely used, and, with these polymers, chemically stable, flexible and mechanically strong films can be

produced.

Other polymers used for the polymer gel electrolyte further include copolymers of methacrylate and ethylene oxides. A gel electrolyte layer can be formed by casting a solution comprising a mixed solution of ethyl methacrylate, ethylene glycol dimethacrylate, and polyethylene oxides of molar weight 10000 or less, an organic solution and a polymerization initiator, onto positive electrode and negative electrodes and directly polymerizing it on the electrodes by using heat or irradiating ultraviolet lights.

The electrolytic solution to be included in the polymer gel electrolyte is composed of non-aqueous solvents and lithium salts dissolved in them. Examples of non-aqueous solvents include cyclic carbonates such as ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC), and vinylene carbonate (VC); acyclic carbonates such as dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylmethyl carbonate (EMC), and dipropyl carbonate (DPC); aliphatic carboxylates such as methyl formate, methyl acetate, methyl propionate, and ethyl propionate; gamma-lactones such as gamma-butyrolactone; acyclic ethers such as 1,2-dimethoxy ethane (DME), 1,2-diethoxy ethane (DEE), and ethoxy methoxy ethane (EME); cyclic ethers such as tetrahydrofuran and 2-methyl tetrahydrofuran; and non-protonic organic solvents such as dimethyl sulfoxide, 1,3-dioxolane, formamide, acetamide, dimethyl formamide, dioxolane, acetonitrile, propyl nitrile, nitromethane, ethyl monoglime, triester phosphate, trimethoxy methyne, dioxolane derivatives, sulfolane, methyl sulfolane, 1,3-dimethyl-2-imidazolidinone, 3-methyl-2-oxazolidinone, propylene carbonate derivatives, tetrahydrofuran derivatives, ethyl ether, 1,3-propane saltane, anisole, dimethyl sulfoxide and N-methyl pyrrolidone. These solvents are used independently or as a mixture of two or more solvents. Mixtures of cyclic carbonate and acyclic carbonate, or cyclic carbonate, acyclic carbonate and aliphatic carboxylate are especially favorable.

Lithium salts which dissolve into the foregoing solvents include LiClO_4 , LiBF_4 , LiPF_6 , LiAlCl_4 , LiSbF_6 , LiSCN , LiCl , LiCF_3SO_3 , LiCF_3CO_2 , $\text{Li}(\text{CF}_3\text{SO}_2)_2$, LiAsF_6 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, $\text{LiB}_{10}\text{Cl}_{10}$, lithium salt of lower aliphatic

carboxylic acid, LiCl, LiBr, LiI, chloroborane lithium, 4-phenil boric acid, and an imide derivatives. These lithium salts can be dissolved individually or as a mixture of two or more in the non-aqueous solvents mentioned earlier, and used as an electrolytic solution. It is preferable to include LiPF_6 in the electrolytic solution.

Especially favorable non-aqueous electrolytic solutions of the present invention include at least ethylene carbonate and ethyl methyl carbonate, and as a supporting salt, LiPF_6 . The amount of the electrolytic solution to be added to the battery is not specifically defined. Considering the amount of the positive electrode and the negative electrode materials and the size of the battery, the required amount can be used. The amount of the supporting electrolytes to be dissolved against the non-aqueous electrolytes is not specifically defined, however, 0.2-2mol/l is favorable, and particularly, 0.5-1.5mol/l is preferable.

It is effective to add other compounds to the electrolytic solution in order to improve discharge and charge/discharge properties. Such compounds include triethyl phosphite, triethanolamine, cyclic ethers, ethylenediamine, n-grime, pyridine, hexaphosphic acid triamide, nitrobenzene direvatives, crown ethers, quaternary ammonium salt, and ethylene glycol dialkyl ether.

In the separator section of the battery of the present invention, structural reinforcements such as particulate dispersants, fillers, non-woven cloths and the like are included. As the structural reinforcements, any particulates and fiber materials which do not chemically change by reacting with organic electrolytic solutions and polymer materials can be used. Especially, silica whose surface is modified with hydrophobic properties (for example by silane coupling treatments), particulates of oxides of such materials as alumina (particle diameter of $1\mu\text{m}$ or less), fibers and non-woven cloths of olefin polymers such as polypropylene and polyethylene can be used. The amount of the structural reinforcements to be added is not particularly limited however, a favorable amount is within the range of 0-40wt% of the separator section comprising polymer gel electrolytes.

By combining novel negative electrode materials and polymer

materials of the present invention, lithium polymer secondary batteries with superior cycle properties and reliability and high energy density can be achieved.

Besides the foregoing polymer gel electrolytes, the present invention can also use lithium ion conductive glass-type solid electrolytes (hereinafter, solid electrolyte).

The solid electrolyte of the present invention is synthesized with three components comprising ; at least lithium sulfide as a first component, one or more compounds selected from a group comprising silicon sulfides, phosphor sulfides and boron sulfides as a second component, and at least one compound selected from lithium phosphate, lithium sulfate, lithium borate, lithium silicate as a third component. The composition ratio of the solid electrolytes at the time of synthesis is not specifically limited on the grounds that synthesized material is in the form of glass, has ionic conductivity of lithium ions and its oxidative decomposition voltage is higher than the voltage at which the battery is used.

The solid electrolytes of the present invention is highly thermally stable with the glass transition temperature being 300°C or higher, and the crystallization temperature, 400°C or higher. As such, when the battery is stored at high temperatures, the generation of gas and degradation of the properties are extremely small. Since the solid electrolytes are in the form of glass, conduction paths of lithium ions are different from those of crystalline solid electrolytes; the paths are isotropic and conductivity can be obtained at any surface of the solid electrolyte powder. Therefore, when mixed with the electrode materials in powder form, contacting surfaces can be set freely.

When the solid electrolytes include oxo-acid salts as a third component, oxidative decomposition resistance voltage is increased to almost 10V, significantly higher compared with those to which oxo-acid salts are not added. The reason for this is assumed to be that when oxo-acid salts are not added, the glass skeleton is composed of Si-S-Si, whereas when the salts are added, in some part, an Si-O-Si skeleton whose Si-O bonding is stronger than Si-S bonding, is formed. Thus, the solid electrolytes of the present invention have high bonding strength, therefore, they can be used with positive electrode materials which

generate voltage as high as 4V or more.

When oxo-acid salts are not added, and the solid electrolytes come into contact with lithium metal, the impedance at the contacting surfaces increases over time. However, by adding oxo-acid salts, the increase in impedance which occurs when the solid electrolytes come in contact with lithium metal, is restricted. Thus, the solid electrolytes of the present invention have an increased stability against contact with lithium metal.

By combining the foregoing negative electrode materials and the solid electrolytes of the present invention, high-capacity batteries with secure reliability in wider range of temperatures and superior cycle properties are achieved.

Constructions of the batteries of the present invention is described below using representative flat-type and cylindrical batteries for example in accordance with preferred embodiments. The present invention is not limited to these embodiments.

The first preferred embodiment

Fig. 1 shows a cross section of a flat-type non-aqueous electrolyte battery. The battery comprises:

- a battery casing 1 made with an aluminum laminate;
- a welding seal for leads 2;
- an aluminum positive electrode lead 3;
- a positive electrode plate 5 using lithium composite oxides as an active material;
- a separator section 6 of gel polymer electrolytes comprising polymer materials such as polyethylene oxides, an electrolytic solution and structural reinforcements;
- a negative electrode plate 7 using composite particles of the present invention as an active material; and
- a copper negative electrode lead 4.

For a polymer material of the gel polymer electrolytes, polyethylene oxides (PEO) whose molecular weight is between 800,000 and 2 million.

PEO is used by dissolving it in a mixed solution of acetone and ethylene carbonate (EC). Further, the composite particles of the present invention, which function as an active material and carbon black used as a conductive material are mixed and dispersed into the foregoing solution to form a paste. The paste is coated onto a copper core material used as a negative electrode current collector. The solvents are then dried and removed from the paste, and then it is cut into a predetermined size to form the negative electrode plate 7.

The positive electrode plate 5 is prepared such that the paste which is formed by mixing and dispersing LiCoO_2 and carbon black in the foregoing PEO solution, is coated on an aluminum core material which functions as a positive electrode current collector, and then processed in the same manner as the negative electrode plate 7.

The separator section 6 is produced in such a manner that PEO is dissolved in an organic electrolytic solution by heating. A polypropylene non-woven fabric functioning as a structural reinforcement, is then used to absorb the solution. Finally the items are cooled to form a gel electrolytic layer.

The positive electrode plate 5, the separator section 6 and the negative electrode plate 7 are laminated under pressure to form an electrode group which is then put inside the battery casing 1. The laminated film around the opening is then thermally welded to obtain a flat-type battery. If gelation or lamination of the electrodes and the separator section is not adequate, a heating process can be applied before sealing the opening.

As the electrolytic solution, LiPF_6 is dissolved into a solvent of EC and EMC mixed in a ratio of 1:1 by volume, at the concentration of 1.0mol/l LiPF_6 .

The batteries of the present invention are charged with a constant current of 5mA until their voltage becomes 4.1V, and then discharged at the constant current of 5mA until their voltage becomes 2.0V at 20°C. The charge/discharge cycle is repeated 100 times, and the ratio of the discharge

capacity at the 100th cycle to that of the initial cycle is shown in Table 2 as the capacity retention rates.

For comparison, a battery is prepared in the same manner as the first preferred embodiment by using spherical graphite as a negative electrode material, and PEO as a polymer material. Results are shown in Table 2.

As shown in Table 2, the use of the polymer gel electrolytes and the composite particles of the present invention achieves non-aqueous electrolyte secondary batteries which have higher energy density and a higher capacity compared with the battery with conventional carbon materials, and also enjoy superior cycle properties and reliability.

The second preferred invention

Instead of the polymer material in the first preferred embodiment, a copolymer of vinylidene fluoride - hexafluoropropylene (PVDF-HFP) is used. A composite particle material C and carbon black which is a conductive material, are mixed with PVDF-HFP, and then mixed and dispersed in a mixed solution of N-methyl pyrrolidone and a dibutyl phthalate to form a paste. The paste is coated onto a copper core material used as a negative electrode current collector, and then dried before being cut into a predetermined size to form the negative electrode plate. The positive electrode plate is prepared such that paste, which is formed by mixing and dispersing LiCoO_2 , carbon black and PVDF-HFP into the mixed solution of N-methyl pyrrolidone and a dibutyl phthalate, is coated onto an aluminum core material which functions as a positive electrode current collector, and then processed in the same manner as the negative electrode plate. Separators are produced such that PVDF-HFP and silicon oxide particulates having hydrophobic properties, and which function as a structural reinforcement, are dispersed into the foregoing mixed solution to obtain a paste dispersion. The paste dispersion is coated and dried. The positive electrode plate, the separators and the negative electrode plate are then welded by a heated roller. Diethyl ether is used in order to have dibutyl phthalate, a plasticizer, dissolve into

it so as to obtain a porous polymer electrode group. This electrode group is then placed into the battery casing 1 before being injected with the organic electrolytic solution used in the first preferred embodiment in order to form a gel polymer electrolyte. To complete, the laminated film around the opening is thermally welded.

An evaluation of the batteries is shown in Table 2. As shown in Table 2, by using the polymer gel electrolytes and the composite particles of the present invention, a high-energy density non-aqueous electrolyte secondary battery with a higher capacity than the battery with conventional carbon materials, and with superior cycle properties and reliability can be achieved.

The third preferred embodiment

Instead of the polymer material in the first preferred embodiment, a polyacrylonitrile (PAN) is used as a polymer material. The composite particle of the present invention and carbon black, a conductive material are mixed and dispersed into a solution prepared by dissolving PAN into dimethyl formamide, a solvent, to form a paste. The paste is coated onto a copper core material used as a negative electrode current collector to obtain the negative electrode plate. The positive electrode plate is produced by using a paste prepared by mixing and dispersing LiCoO_2 , carbon black and PAN. The positive and the negative electrode plates are washed with acetone or ethanol to remove dimethyl formamide.

A non-woven fabric like film made of PAN is used for the separators.

The positive electrode plate, the separators and the negative electrode plate are laminated to form an electrode group. The organic electrolytic solution used in the first preferred embodiment is injected into the electrode group which is then sandwiched between hot plates and heated under pressure before being cooled down. By this process, the electrode group is integrated and the electrolytic solution gels. The electrode group is then placed in the battery casing 1 and sealed.

An evaluation of the batteries is shown in Table 2. As shown in Table 2, by using the polymer gel electrolytes and the composite particles of the present invention, a high-energy density non-aqueous electrolyte secondary battery with a higher capacity than the battery with conventional carbon materials, and with superior cycle properties and reliability can be achieved.

The fourth preferred embodiment

Instead of the polymer material in the first preferred embodiment, polyester polymers (PET) which are copolymers of polybutylene terephthalate and ethyl methacrylate, are used as a polymer material. The polymer material is dissolved in a mixed solvent of formic acid and ethyl acetate. A composite particle material C and carbon black are then added to the mixed solvent to form a paste. Subsequently, the paste is coated onto a core material and dried to form the negative electrode plate in the same manner as the first preferred embodiment.

The positive electrode plate is produced by using a paste prepared by mixing and dispersing LiCoO_2 , carbon black and PET.

To prepare the separators, a polypropylene non-woven fabric which acts as a structural reinforcement is used to absorb PET, and then, in order to make the separators porous, it is dried and the solvents are removed.

The positive electrode plate, the separators and the negative electrode plate are laminated to form an electrode group. The organic electrolytic solution used in the first preferred embodiment is injected into the electrode group which is then sandwiched between hot plates and heated under pressure before being cooled down. By this process, the electrode group is integrated and the electrolytic solution gels. The electrode group is then placed in the battery casing 1 and sealed.

An evaluation of the batteries is shown in Table 2. As shown in Table 2, by using the polymer gel electrolytes and the composite particles of the present invention, a high-energy density non-aqueous electrolyte secondary battery with

a higher capacity than the battery with conventional carbon materials, and also with superior cycle properties and reliability can be achieved.

The fifth preferred embodiment

5

Instead of the polymer material in the first preferred embodiment, a polymer material, an aqueous solution including a Na⁺ ion crosslinked body of an ethylene - methacrylic acid copolymer as a binder and a carboxymethyl cellulose as a thickener, is used. The composite particles of the present invention and carbon black are mixed and dispersed in the aqueous solution to form a paste. The paste is then used to prepare the negative electrode plate. The foregoing solution is also used to prepare the positive electrode plate.

Subsequently, a solution comprising a mixed solution of ethylene glycol dimethacrylate and polyethylene oxides of molecular weight of 10,000 or less, the organic electrolytic solution, the same as that of the first preferred embodiment, a photo-polymerization initiator and a polypropylene filler, used as a structural reinforcement, is cast on the positive and the negative plates. Ultraviolet lights are then irradiated onto the electrode plates in an argon atmosphere. In this manner, the material with the foregoing composition is photo-polymerized directly to form a gel electrolyte layer (PMMA-PEO) on the surfaces of the electrode plates which are then laminated.

An evaluation of the batteries is shown in Table 2. As shown in Table 2, by using the polymer gel electrolytes and the composite particles of the present invention, a high-energy density non-aqueous electrolyte secondary battery with a higher capacity than the battery with conventional carbon materials, and also with superior cycle properties and reliability can be achieved.

The polymer gel electrolytes used in the first to fifth preferred embodiments have ionic conductivity of 10^{-3} S/cm level.

30

The sixth preferred embodiment

Fig. 6 shows a vertical cross section of a cylindrical battery of the present invention. The positive electrode plate 5 and the negative electrode plate 6 are spirally rolled a plurality of times via the separator 7, and placed in the battery casing 1. Coming out from the positive electrode plate 5 is a positive electrode lead 5a which is connected to a sealing plate 2. In the same manner, a negative electrode lead 6a comes out from a negative electrode plate 6, and is connected to the bottom of the battery casing 1.

Electronically conductive metals and alloys having organic electrolytic solution resistance can be used for the battery casing and lead plates. For example, such metals as iron, nickel, titanium, chromium, molybdenum, copper and aluminum and their alloys can be used. For the battery casing, stainless steel plate or processed Al-Mn alloy plate, and for the positive electrode lead and the negative electrode lead, respectively aluminum and nickel are most preferably used. For the battery casing, engineering plastics can be used independently or with metals in order to reduce weight.

Insulating rings 8 are disposed on the top and the bottom of an electrode plate group 4. A safety valve can be used as a sealing plate. Apart from the safety valve, other conventionally used safety elements can be adopted. As an anti-overcurrent element, for example, fuses, bimetal and PTC elements can be used. To deal with increases in internal pressure of the battery casing, a cut can be provided to the battery casing, a gasket cracking method or a sealing plate cracking method can be applied, or the connection to the lead plate can be severed. As other methods, a protective circuit incorporating anti-overcharging and anti-overdischarging systems, can be included in or connected independently to a charger. As an anti-overcharging method, a system to cut off a current by utilizing an increase in internal pressure of the battery. In this case, a compound which raises internal pressure can be mixed with the composites or with the electrolytes. Such compounds include carbonates such as Li_2CO_3 , LiHCO_3 , Na_2CO_3 , NaHCO_3 , CaCO_2 and MgCO_3 .

The cap, the battery casing, the sheet and the lead plate can be welded by well-known methods (such as an alternative current or a direct current electric

welding, a laser welding and an ultrasonic welding). As a sealing material for the opening, conventional compounds and composites such as asphalt can be used.

A preferred embodiment wherein a cylindrical battery using solid electrolytes for separators is described below.

(A manufacturing method of the solid electrolytes and a solid electrolyte sheet)

Lithium ion conductive glass-type solid electrolytes are manufactured in steps described below.

Lithium phosphate, lithium sulfide, and silicon disulfide are mixed at a molar ratio of 1:63:36, then put in a glassy carbon crucible and fused at 1000°C for two hours in a dry nitrogen atmosphere. The fused fluid is quenched by a two-roller, and the resultant solid electrolytic glass is ground to form solid electrolyte powder. In the same manner, other solid electrolytes are synthesized with different combination of ingredients. The result is shown in Table 3. The ionic conductivity and the oxidative decomposition resistance voltage in the Table represent values measured respectively by the AC impedance method and the potential scanning method.

Subsequently, 2wt% of PTFE is added to 98wt% of the solid electrolyte powder and mixed thoroughly in a mortar to make it elastic. The elastic body is then pressed and rolled by a roller, and a solid electrolytic sheet is obtained.

(negative electrode plate)

To prepare the negative electrode plate 6, 15wt% of the solid electrolyte powder, 20wt% of carbon powder and 5wt% of PVDF are mixed with 60wt% of the composite particles synthesized in the foregoing manner. The mixture is dispersed in dehydrated N-methyl pyrrolidinone to form a slurry. The slurry is coated onto a negative electrode current collector comprising copper foil, dried and rolled under pressure.

(positive electrode plate)

To prepare the positive electrode plate 5, 15wt% of the solid electrolytic powder, 10wt% of carbon powder and 5wt% of PVDF are mixed with 70wt% of LiOCo_2 powder. The mixture is dispersed in dehydrated N-methyl pyrrolidinone to form a slurry. The slurry is coated onto a positive electrode current collector comprising aluminum foil, and dried and rolled under pressure

In the foregoing manner, batteries are constructed by using the materials shown in Table 1 for the negative electrode and materials a-l shown in Table 3 for the solid electrolytes. These cylindrical batteries are 18mm in diameter and 65mm in height. The batteries are charged with constant current of 100mA until their voltage becomes 4.1V, and then discharged at the constant current of 100mA until their voltage becomes 2.0V. The charge/discharge cycle is repeated 100 times, and ratio of the discharge capacity at the 100th cycle to that of the first cycle is shown in Table 4 as capacity retention rates.

Table 4 also shows capacity retention rates gained by comparing the initial capacity measured after the batteries of the same construction are charged with constant current of 100mA until their voltage becomes 4.1V and discharged at the constant current of 100mA until their voltage becomes 2.0V, and the capacity measured when the same batteries are charged again on the same condition until their voltage becomes 4.1V and stored for 60 days at 85°C. The capacity retention rate after the storing is a ratio of the discharge capacity after storing to the discharge capacity before storing.

For comparison, batteries using graphite or an Al-Li alloy for negative electrodes are prepared and tested.

To check whether the gas is produced after storing, a hole is made on the battery and gas is collected in a liquid paraffin. No gas is collected from any batteries. Thus, it can be concluded that none of the batteries of the present invention produced gas.

As Table 4 shows, the batteries of the present invention has a higher capacity, and superior cycle properties, high-rate charge/discharge properties and

high-temperature storing properties compared with the batteries using conventional carbon materials and Al-Li alloys as negative electrode materials.

The composition of the solid electrolyte of this embodiment is not specifically defined on the condition that the resultant material is glassy, and has
5 an ionic conductivity for lithium ions and the oxidative decomposition voltage of 5V or higher. The solid electrolytes of this embodiment is not specifically defined in terms of their composition.

The battery of the present invention can be applied in any form including coins, buttons, sheets, laminates, cylinders, flat types, square types and
10 large types used in electric cars.

The battery of the present invention can be used for portable information terminals, portable electronic devices, small size domestic electricity storing devices, motor cycles, electric cars and hybrid electric cars. However, the application of the battery is not limited to the foregoing.
15

Industry Applicability

The batteries using the non-aqueous electrolytes and the composite particles for the negative electrode of the present invention have a higher
20 capacity and superior cycle properties, high-rate charge/discharge properties and high-temperature storage properties. As such, the batteries of the present invention can be used in portable information terminals, portable electronic devices, small size domestic electricity storing devices, motor cycles, electric cars and hybrid electric cars, thereby offering remarkable benefits when
25 industrially applied.

Table 1

Negative electrode material	Phase A	Phase B	Melting temperature (°C)	Solid phase line temperature (°C)	Composition (Atom %)
Material A	Sn	Mg ₂ Sn	770	204	Sn:Mg=50:50
Material B	Sn	FeSn ₂	1540	513	Sn:Fe=70:30
Material C	Sn	MoSn ₂	1200	800	Sn:Mo=70:30
Material D	Sn	Zn, Sn Solid S.	420	199	Sn:Zn=90:10
Material E	Sn	Cd, Sn Solid S.	232	133	Sn:Cd=95:5
Material F	Sn	In, Sn Solid S.	235	224	Sn:In=98:2
Material G	Sn	Sn, Pb Solid S.	232	183	Sn:Pb=80:20
Material H	Si	Mg ₂ Si	1415	946	Si:Mg=70:30
Material I	Si	CoSi ₂	1495	1259	Si:Co=85:15
Material J	Si	NiSi ₂	1415	993	Si:Ni=69:31
Material K	Si	Si, Zn Solid S.	1415	420	Si:Zn=50:50
Material L	Si	Si, Al Solid S.	1415	577	Si:Al=40:60
Material M	Si	Si, Sn Solid S.	1415	232	Si:Sn=50:50
Material N	Zn	Mg ₂ Zn ₁₁	650	364	Zn:Mg=92.9:7.8
Material O	Zn	Zn, Cu Solid S.	1085	425	Zn:Cu=97:3
Material P	Zn	VZn ₁₁	700	420	Zn:V=94:6
Material Q	Zn	Zn, Cd Solid S.	420	266	Zn:Cd=50:50
Material R	Zn	Zn, Al Solid S.	661	381	Zn:Al=90:10
Material S	Zn	Zn, Ge Solid S.	938	394	Zn:Ge=97:3

Table 2

Example		Negative electrode materials	Initial Discharge Capacity (mAh)	100th Discharge Capacity (mAh)	capacity retention rate (%)
Example 1	1	Material A	1 4 8	1 3 3	9 0
	2	B	1 4 7	1 3 1	8 9
	3	C	1 4 6	1 2 8	8 8
	4	D	1 4 6	1 3 1	9 0
	5	E	1 4 8	1 3 5	9 1
	6	F	1 4 7	1 3 4	9 1
	7	G	1 4 8	1 3 3	9 0
	8	H	1 5 0	1 3 5	9 0
	9	I	1 4 9	1 3 3	8 9
	10	J	1 5 2	1 3 8	9 1
	11	K	1 5 1	1 3 6	9 0
	12	L	1 5 3	1 3 5	8 8
	13	M	1 5 2	1 3 7	9 0
	14	N	1 4 9	1 3 6	9 1
	15	O	1 5 0	1 3 5	9 0
	16	P	1 4 6	1 3 0	8 9
	17	Q	1 4 7	1 3 2	9 0
	18	R	1 5 0	1 3 5	9 0
	19	S	1 4 7	1 3 1	8 9
Example 2	1	Material A	1 5 0	1 3 5	9 0
	2	J	1 5 3	1 3 8	9 0
	3	N	1 5 0	1 3 7	9 1
Example 3	1	Material A	1 4 7	1 3 1	8 9
	2	J	1 5 1	1 3 6	9 0
	3	N	1 5 2	1 3 5	8 9
Example 4	1	Material A	1 4 7	1 3 2	9 0
	2	J	1 4 8	1 3 3	9 0
	3	N	1 4 6	1 3 1	9 0
Example 5	1	Material A	1 4 8	1 3 3	9 0
	2	J	1 5 0	1 3 5	9 0
	3	N	1 5 1	1 3 6	9 0
Comparative Example PEO		Graphite	1 1 6	1 0 7	9 2

Table 3

Solid Electrolyte	Composition	Ion conductivity mS/cm	Oxidative Decomposition Voltage V vs Li ⁺ /Li
a	0.01Li ₃ PO ₄ /0.63Li ₂ S/0.36SiS ₂	1.8	1.0
b	0.02Li ₂ SO ₄ /0.63Li ₂ S/0.35SiS ₂	1.6	9.5
c	0.01Li ₃ BO ₃ /0.63Li ₂ S/0.36SiS ₂	1.5	1.0
d	0.01Li ₄ SiO ₄ /0.63Li ₂ S/0.36SiS ₂	1.3	9.0
e	0.01Li ₃ PO ₄ /0.63Li ₂ S/0.36P ₂ S ₅	1.6	1.0
f	0.02Li ₂ SO ₄ /0.63Li ₂ S/0.35P ₂ S ₅	1.4	9.7
g	0.01Li ₃ BO ₃ /0.63Li ₂ S/0.36P ₂ S ₅	1.1	1.0
h	0.01Li ₄ SiO ₄ /0.63Li ₂ S/0.36P ₂ S ₅	1.0	9.3
i	0.01Li ₃ PO ₄ /0.63Li ₂ S/0.36B ₂ S ₃	1.7	1.0
j	0.02Li ₂ SO ₄ /0.63Li ₂ S/0.35B ₂ S ₃	1.5	9.3
k	0.01Li ₃ BO ₃ /0.63Li ₂ S/0.36B ₂ S ₃	1.3	9.9
l	0.01Li ₄ SiO ₄ /0.63Li ₂ S/0.36B ₂ S ₃	1.2	9.1

Table 4

Battery	Solid electrolyte	Negative Electrode Material	Initial Discharge Capacity (mAh)	100th Discharge Capacity (mAh)	Cycle capacity retention rate (%)	Capacity retention rate (%)
1	a	Material A	1 4 9 8	1 4 9 5	9 9 . 8	9 9 . 9
2		B	1 4 9 1	1 4 8 8	9 9 . 8	9 9 . 9
3		C	1 4 7 8	1 4 7 7	9 9 . 9	9 9 . 9
4		D	1 4 8 2	1 4 8 2	1 0 0	1 0 0
5		E	1 5 0 0	1 4 9 7	9 9 . 8	9 9 . 9
6		F	1 4 8 9	1 4 8 5	9 9 . 7	9 9 . 8
7		G	1 4 9 7	1 4 9 4	9 9 . 8	1 0 0
8		H	1 5 6 5	1 5 6 0	9 9 . 7	1 0 0
9		I	1 5 5 2	1 5 5 1	9 9 . 9	1 0 0
10		J	1 5 7 9	1 5 7 7	9 9 . 9	9 9 . 9
11		K	1 5 7 5	1 5 7 1	9 9 . 7	9 9 . 9
12		L	1 5 9 1	1 5 8 8	9 9 . 8	1 0 0
13		M	1 5 9 1	1 5 8 9	9 9 . 9	1 0 0
14		N	1 5 5 1	1 5 4 9	9 9 . 9	1 0 0
15		O	1 5 5 6	1 5 5 6	1 0 0	9 9 . 9
16		P	1 5 2 1	1 5 2 0	9 9 . 9	1 0 0
17		Q	1 5 2 8	1 5 2 7	9 9 . 9	1 0 0
18		R	1 5 5 9	1 5 5 7	9 9 . 9	9 9 . 9
19		S	1 5 2 6	1 5 2 4	9 9 . 9	1 0 0
Comparative	a	Graphite	1 2 0 8	1 2 0 4	9 9 . 7	9 9 . 9
		Al-Li alloy	1 4 9 3	7 0 4	4 7 . 2	9 9 . 2
1	b	Material A	1 4 9 6	1 4 9 2	9 9 . 7	9 9 . 5
2		B	1 4 8 8	1 4 8 5	9 9 . 8	9 9 . 7
3		C	1 4 7 6	1 4 7 2	9 9 . 7	9 9 . 8
4		D	1 4 8 2	1 4 8 1	9 9 . 9	9 9 . 4
5		E	1 4 9 7	1 4 9 7	1 0 0	9 9 . 3
6		F	1 4 8 8	1 4 8 5	9 9 . 8	9 9 . 7
7		G	1 4 9 2	1 4 8 8	9 9 . 6	9 9 . 6
8		H	1 5 6 1	1 5 5 9	9 9 . 9	9 8 . 9
9		I	1 5 5 0	1 5 5 0	1 0 0	9 9 . 9
10		J	1 5 7 4	1 5 7 1	9 9 . 8	9 9 . 2
11		K	1 5 7 5	1 5 7 0	9 9 . 7	9 9 . 3
12		L	1 5 8 8	1 5 8 5	9 9 . 8	9 9 . 4
13		M	1 5 8 9	1 5 8 9	1 0 0	9 9 . 9
14		N	1 5 4 8	1 5 4 6	9 9 . 9	9 9 . 3

15		O	1 5 5 0	1 5 4 5	99. 7	99. 4
16		P	1 5 1 6	1 5 0 7	99. 4	99. 6
17		Q	1 5 2 3	1 5 0 8	99. 0	99. 2
18		R	1 5 5 5	1 5 4 7	99. 5	99. 1
19		S	1 5 2 1	1 5 0 9	99. 2	98. 8
comparative	b	Graphite	1 2 0 2	1 1 9 8	99. 7	98. 9
		Al-Li alloy	1 4 8 9	6 8 9	46. 3	99. 0
1	c	Material A	1 4 8 7	1 4 8 0	99. 5	99. 0
2		B	1 4 8 0	1 4 7 9	99. 9	98. 9
3		C	1 4 6 7	1 4 6 0	99. 5	98. 8
4		D	1 4 7 1	1 4 5 9	99. 2	98. 2
5		E	1 4 8 9	1 4 7 7	99. 2	99. 3
6		F	1 4 7 8	1 4 6 2	98. 9	98. 9
7		G	1 4 8 6	1 4 7 0	98. 9	99. 1
8		H	1 5 5 4	1 5 4 2	99. 2	99. 3
9		I	1 5 4 1	1 5 3 0	99. 3	1 0 0
10		J	1 5 6 8	1 5 6 3	99. 7	99. 7
11		K	1 5 6 4	1 5 6 0	99. 7	99. 3
12		L	1 5 8 0	1 5 7 7	99. 8	99. 0
13		M	1 5 7 9	1 5 7 1	99. 5	98. 8
14		N	1 5 4 0	1 5 3 2	99. 5	98. 7
15		O	1 5 4 5	1 5 3 4	99. 3	98. 9
16		P	1 5 1 0	1 5 0 1	99. 4	99. 1
17		Q	1 5 1 7	1 5 1 2	99. 7	99. 3
18		R	1 5 4 8	1 5 4 0	99. 5	99. 2
19		S	1 5 1 5	1 5 0 5	99. 3	99. 4
comparative	c	Graphite	1 1 9 7	1 1 9 0	99. 4	99. 7
		Al-Li alloy	1 4 8 2	6 8 2	46. 0	99. 3
1	d	Material A	1 4 9 4	1 4 8 5	99. 4	99. 3
2		B	1 4 8 7	1 4 8 0	99. 5	99. 1
3		C	1 4 7 4	1 4 6 5	99. 4	99. 6
4		D	1 4 7 8	1 4 6 9	99. 4	99. 7
5		E	1 4 9 6	1 4 8 5	99. 3	98. 8
6		F	1 4 8 5	1 4 7 2	99. 1	99. 4
7		G	1 4 9 3	1 4 8 0	99. 1	1 0 0
8		H	1 5 6 1	1 5 4 9	99. 2	99. 9
9		I	1 5 4 8	1 5 3 5	99. 2	99. 8
10		J	1 5 7 5	1 5 6 0	99. 0	99. 3
11		K	1 5 7 0	1 5 5 7	99. 2	99. 1
12		L	1 5 8 7	1 5 6 9	98. 9	99. 4
13		M	1 5 8 6	1 5 7 1	99. 1	98. 7

14		N	1 5 4 7	1 5 3 0	98. 9	98. 9
15		O	1 5 5 2	1 5 3 9	99. 2	99. 3
16		P	1 5 1 7	1 5 0 1	98. 9	98. 9
17		Q	1 5 2 4	1 5 1 1	99. 1	1 0 0
18		R	1 5 5 5	1 5 4 2	99. 2	99. 4
19		S	1 5 2 2	1 5 0 8	99. 1	99. 7
comparative	d	Graphite	1 2 0 4	1 1 9 7	99. 4	99. 2
		Al-Li alloy	1 4 8 9	6 7 3	45. 2	99. 3
1	e	Material A	1 4 9 2	1 4 7 7	99. 0	98. 9
2		B	1 4 8 5	1 4 6 9	98. 8	98. 4
3		C	1 4 7 2	1 4 5 5	98. 8	98. 6
4		D	1 4 7 6	1 4 5 7	98. 7	98. 4
5		E	1 4 9 4	1 4 8 0	99. 1	99. 4
6		F	1 4 8 3	1 4 6 7	98. 9	99. 1
7		G	1 4 9 1	1 4 7 5	98. 9	98. 6
8		H	1 5 5 9	1 4 4 2	98. 9	98. 5
9		I	1 5 4 6	1 5 3 0	99. 0	98. 4
10		J	1 5 7 3	1 5 5 9	99. 1	98. 7
11		K	1 5 6 9	1 5 5 3	99. 0	99. 8
12		L	1 5 8 5	1 5 6 9	99. 0	1 0 0
13		M	1 5 8 4	1 5 7 2	99. 2	99. 3
14		N	1 5 4 5	1 5 2 9	99. 0	98. 7
15		O	1 5 5 0	1 5 3 8	99. 2	98. 6
16		P	1 5 1 5	1 5 0 0	99. 0	99. 2
17		Q	1 5 2 2	1 5 1 0	99. 2	98. 9
18		R	1 5 5 3	1 5 4 1	99. 2	98. 5
19		S	1 5 2 0	1 5 0 3	98. 9	98. 8
comparative	e	Graphite	1 2 0 2	1 1 8 9	98. 9	98. 7
		Al-Li alloy	1 4 8 7	6 6 9	45. 0	99. 7
1	f	Material A	1 4 9 0	1 4 8 0	99. 3	1 0 0
2		B	1 4 8 3	1 4 7 2	99. 3	99. 9
3		C	1 4 7 0	1 4 5 7	99. 1	98. 9
4		D	1 4 7 4	1 4 6 0	99. 1	99. 3
5		E	1 4 9 2	1 4 7 9	99. 1	99. 4
6		F	1 4 8 1	1 4 6 6	99. 0	1 0 0
7		G	1 4 8 9	1 4 7 2	98. 9	99. 3
8		H	1 5 5 7	1 5 4 2	99. 0	99. 2
9		I	1 5 4 4	1 5 3 0	99. 1	98. 8
10		J	1 5 7 1	1 5 5 4	98. 9	98. 7
11		K	1 5 6 6	1 5 4 9	98. 9	99. 0
12		L	1 5 8 3	1 5 6 0	98. 5	1 0 0

13		M	1 5 8 2	1 5 6 8	99. 1	99. 3
14		N	1 5 4 3	1 5 3 0	99. 2	98. 7
15		O	1 5 4 8	1 5 3 2	99. 0	98. 3
16		P	1 5 1 3	1 4 9 7	98. 9	98. 1
17		Q	1 5 2 0	1 5 0 0	98. 7	98. 4
18		R	1 5 5 1	1 5 3 5	99. 0	99. 2
19		S	1 5 1 8	1 4 9 9	98. 7	99. 3
comparative	f	Graphite	1 2 0 0	1 1 8 5	98. 9	98. 1
		Al-Li alloy	1 4 8 5	6 9 7	46. 9	97. 8
1	g	Material A	1 4 8 9	1 4 7 7	99. 2	99. 6
2		B	1 4 8 2	1 4 6 9	99. 1	99. 1
3		C	1 4 6 8	1 4 5 2	98. 9	99. 3
4		D	1 4 7 2	1 4 6 0	99. 2	98. 4
5		E	1 4 9 0	1 4 7 8	99. 2	98. 9
6		F	1 4 8 0	1 4 6 6	99. 1	99. 2
7		G	1 4 8 7	1 4 7 0	98. 9	99. 4
8		H	1 5 5 5	1 5 4 1	99. 1	98. 7
9		I	1 5 4 3	1 5 2 9	99. 1	98. 9
10		J	1 5 6 9	1 5 5 0	98. 8	99. 0
11		K	1 5 6 4	1 5 4 9	99. 0	99. 1
12		L	1 5 8 1	1 5 7 0	99. 3	99. 4
13		M	1 5 8 0	1 5 6 7	99. 2	99. 2
14		N	1 5 4 2	1 5 3 0	99. 2	1 0 0
15		O	1 5 1 7	1 5 0 0	98. 9	99. 1
16		P	1 5 1 0	1 4 9 7	99. 1	99. 7
17		Q	1 5 1 8	1 5 0 2	98. 9	98. 3
18		R	1 5 4 9	1 5 3 0	98. 9	98. 8
19		S	1 5 1 7	1 4 9 9	98. 8	99. 0
comparative	g	Graphite	1 1 9 8	1 1 8 0	98. 5	99. 8
		Al-Li alloy	1 4 8 2	6 7 7	45. 7	99. 3
1	h	Material A	1 4 9 5	1 4 7 9	98. 9	99. 1
2		B	1 4 9 0	1 4 7 7	99. 1	99. 2
3		C	1 4 7 2	1 4 5 1	98. 6	98. 3
4		D	1 4 7 9	1 4 6 8	99. 3	99. 3
5		E	1 4 9 6	1 4 8 1	99. 0	98. 9
6		F	1 4 8 6	1 4 7 2	99. 1	99. 2
7		G	1 4 9 3	1 4 7 2	98. 6	98. 6
8		H	1 5 6 1	1 5 4 0	98. 7	98. 4
9		I	1 5 4 9	1 5 3 0	98. 8	98. 7
10		J	1 5 7 5	1 5 5 7	98. 9	99. 0
11		K	1 5 6 9	1 5 5 0	98. 8	99. 3

12		L	1 5 8 7	1 5 7 0	98. 9	99. 4
13		M	1 5 8 6	1 5 6 9	98. 9	99. 2
14		N	1 5 4 8	1 5 4 0	99. 5	99. 0
15		O	1 5 2 2	1 5 0 2	98. 7	98. 8
16		P	1 5 1 6	1 5 0 0	98. 9	99. 1
17		Q	1 5 2 4	1 5 0 9	99. 0	99. 3
18		R	1 5 5 5	1 5 3 8	98. 9	99. 0
19		S	1 5 2 4	1 5 0 9	99. 0	98. 7
comparative	h	Graphite	1 2 0 7	1 1 8 8	98. 4	99. 2
		Al-Li alloy	1 4 9 0	7 1 4	47. 9	98. 9
1	i	Material A	1 5 0 1	1 4 9 8	99. 8	99. 7
2		B	1 4 9 6	1 4 9 4	99. 9	99. 6
3		C	1 4 7 8	1 4 7 0	99. 5	99. 2
4		D	1 4 8 4	1 4 7 7	99. 5	99. 0
5		E	1 5 0 1	1 4 9 0	99. 3	99. 4
6		F	1 4 9 2	1 4 7 9	99. 1	98. 7
7		G	1 4 9 9	1 4 7 9	98. 7	98. 8
8		H	1 5 6 7	1 5 6 1	99. 6	99. 1
9		I	1 5 4 7	1 5 2 9	98. 8	99. 0
10		J	1 5 8 0	1 5 6 1	98. 9	99. 2
11		K	1 5 6 7	1 5 6 1	99. 0	99. 4
12		L	1 5 9 2	1 5 7 0	98. 6	98. 9
13		M	1 5 9 1	1 5 7 1	98. 7	98. 9
14		N	1 5 5 3	1 5 4 7	99. 6	99. 1
15		O	1 5 2 9	1 5 0 2	98. 2	99. 1
16		P	1 5 2 3	1 5 0 5	98. 8	99. 2
17		Q	1 5 3 0	1 5 1 0	98. 7	98. 9
18		R	1 5 6 2	1 5 4 7	99. 0	98. 3
19		S	1 5 3 1	1 5 1 1	98. 7	98. 4
comparative	i	Graphite	1 2 1 2	1 1 9 9	98. 9	99. 2
		Al-Li alloy	1 4 9 6	7 2 1	48. 2	99. 5
1	j	Material A	1 4 9 9	1 4 8 2	98. 9	98. 8
2		B	1 4 9 4	1 4 7 7	98. 9	99. 1
3		C	1 4 7 7	1 4 6 2	99. 0	99. 2
4		D	1 4 8 3	1 4 6 6	98. 9	98. 7
5		E	1 4 9 9	1 4 8 2	98. 9	98. 6
6		F	1 4 9 0	1 4 7 3	98. 9	99. 3
7		G	1 4 9 6	1 4 7 8	98. 9	99. 5
8		H	1 5 6 5	1 5 4 8	98. 9	98. 4
9		I	1 5 4 5	1 5 3 2	99. 2	98. 8
10		J	1 5 7 8	1 5 6 0	98. 9	98. 3

11		K	1 5 7 3	1 5 5 7	98. 9	99. 1
12		L	1 5 8 9	1 5 7 0	98. 8	99. 0
13		M	1 5 8 8	1 5 6 9	98. 8	98. 4
14		N	1 5 5 0	1 5 2 8	98. 6	98. 7
15		O	1 5 2 7	1 5 0 8	98. 8	99. 0
16		P	1 5 1 9	1 5 0 1	98. 8	99. 3
17		Q	1 5 2 6	1 5 1 2	99. 1	99. 1
18		R	1 5 5 9	1 5 4 0	98. 8	98. 6
19		S	1 5 2 8	1 5 1 1	98. 9	98. 7
comparative	j	Graphite	1 2 0 9	1 1 9 1	98. 5	98. 9
		Al-Li alloy	1 4 9 2	7 0 3	47. 1	98. 9
1	k	Material A	1 4 9 3	1 4 7 3	98. 7	98. 9
2		B	1 4 8 8	1 4 6 7	98. 6	99. 1
3		C	1 4 7 1	1 4 5 3	98. 8	99. 3
4		D	1 4 7 7	1 4 5 6	98. 6	98. 8
5		E	1 4 9 3	1 4 7 2	98. 6	98. 8
6		F	1 4 8 4	1 4 6 5	98. 7	98. 6
7		G	1 4 8 9	1 4 6 6	98. 5	98. 9
8		H	1 5 5 8	1 5 3 9	98. 8	98. 7
9		I	1 5 4 0	1 5 2 0	98. 7	99. 0
10		J	1 5 7 1	1 5 5 3	98. 9	98. 8
11		K	1 5 6 7	1 5 4 5	98. 6	98. 5
12		L	1 5 8 2	1 5 6 1	98. 7	98. 5
13		M	1 5 8 1	1 5 6 0	98. 7	98. 7
14		N	1 5 4 1	1 5 1 9	98. 6	98. 7
15		O	1 5 2 0	1 4 9 9	98. 6	99. 3
16		P	1 5 1 2	1 4 9 3	98. 7	99. 7
17		Q	1 5 2 2	1 5 0 3	98. 8	99. 4
18		R	1 5 5 1	1 5 3 1	98. 7	98. 0
19		S	1 5 1 9	1 5 0 0	98. 7	98. 2
comparative	k	Graphite	1 2 0 2	1 1 8 3	98. 4	99. 1
		Al-Li alloy	1 4 8 5	6 8 9	46. 4	99. 2
1	l	Material A	1 4 9 1	1 4 7 2	98. 7	99. 4
2		B	1 4 8 6	1 4 6 0	98. 3	99. 0
3		C	1 4 6 9	1 4 4 3	98. 2	98. 9
4		D	1 4 7 5	1 4 5 2	98. 4	98. 5
5		E	1 4 9 0	1 4 6 8	98. 5	98. 7
6		F	1 4 8 2	1 4 6 0	98. 5	98. 9
7		G	1 4 8 7	1 4 6 2	98. 3	99. 1
8		H	1 5 5 7	1 5 3 5	98. 6	99. 4
9		I	1 5 3 7	1 5 1 1	98. 3	99. 2

10		J	1 5 6 8	1 5 4 6	9 8. 6	9 8. 3
11		K	1 5 6 5	1 5 3 7	9 8. 2	9 8. 7
12		L	1 5 7 9	1 5 6 3	9 9. 0	9 9. 1
13		M	1 5 7 9	1 5 6 1	9 8. 9	9 9. 3
14		N	1 5 3 8	1 5 0 8	9 8. 0	9 8. 1
15		O	1 5 1 6	1 4 9 5	9 8. 6	9 8. 2
16		P	1 5 1 0	1 4 9 1	9 8. 7	9 8. 6
17		Q	1 5 1 9	1 5 0 0	9 8. 7	9 9. 4
18		R	1 5 4 8	1 5 2 5	9 8. 5	9 9. 1
19		S	1 5 1 6	1 4 9 5	9 8. 6	9 9. 2
comparative		Graphite	1 1 9 7	1 1 7 9	9 8. 5	9 8. 9
		Al-Li alloy	1 4 8 0	6 6 6	4 5. 0	9 8. 7

What is claimed is:

1. A non-aqueous electrolyte secondary battery comprising;
 - a positive electrode and a negative electrode capable of intercalating and de-intercalating lithium;
 - a non-aqueous electrolyte solution; and
 - a solid electrolyte,

wherein said negative electrode contains a composite particle constructed such that at least part of a surface of a nuclear particle containing at least one of tin, silicon and zinc as a constituent element is coated with one of;

- a solid solution, and
- an inter-metallic compound,

which are composed of an element included in said nuclear particle and at least one element, exclusive of the element included in said nuclear particle, selected from a group of elements in a Periodic Table, comprising group 2 elements, transition elements, group 12 elements, group 13 elements and group 14 elements exclusive of carbon,

and said solid electrolyte is a polymer gel electrolyte.

2. The non-aqueous electrolyte secondary battery of claim 1, wherein said positive electrode includes a lithium-containing composite oxide and a polymer composing said polymer gel electrolyte, and said negative electrolyte includes said composite particle and a polymer composing said polymer gel electrolyte.

3. The non-aqueous electrolyte secondary battery of one of claim 1 and claim 2 wherein main structure of said polymer is one of polyalkylene oxide and a derivative of the same.

4. The non-aqueous electrolyte secondary battery of one of claim 1

and claim 2 wherein said polymer is one of a polymer and a copolymer including at least one monomer selected from a group comprising acrylonitrile, vinylidene fluoride, hexafluoro-propylene, tetrafluoro-ethylene, and perfluoro-alkyl vinyl ether.

5. The non-aqueous electrolyte secondary battery of one of claim 1 and claim 2, wherein said polymer is a polyester polymer whose main structure is one of polyester and a derivative of the same.

6. The non-aqueous electrolyte secondary battery of one of claim 1 and claim 2, wherein said polymer is a copolymer of methacrylate and an ethylene oxide.

7. The non-aqueous electrolyte secondary battery of one of claim 1 and claim 2, wherein said polymer gel electrolyte includes at least one of structural reinforcements selected from a hydrophobic treated particulate, and a fiber or a non-woven fabric of a polyolefin polymers.

8. A non-aqueous electrolyte secondary battery comprising;
 a positive electrode and a negative electrode capable of
 intercalating and de-intercalating lithium;
 a non-aqueous electrolyte solution; and
 a solid electrolyte,

wherein said negative electrode contains a composite particle constructed such that at least part of a surface of a nuclear particle containing at least one of tin, silicon and zinc as a constituent element is coated with one of;

 a solid solution, and
 an inter-metallic compound,
 which are composed of elements included in said nuclear particle and at least one element, exclusive of the element included in said

nuclear particle, selected from a group of elements in a Periodic Table, comprising group 2 elements, transition elements, group 12 elements, group 13 elements and group 14 elements exclusive of carbon,

and said solid electrolyte is a lithium ion conductive glass-type solid electrolyte.

9. The non-aqueous electrolyte secondary battery of claim 8, wherein said lithium ion conductive glass-type solid electrolyte is synthesized with raw materials including;

a first component including at least a lithium sulfide;

a second component including at least one of a silicon sulfide, a phosphor sulfide and a boron sulfide; and

a third component including at least one of lithium phosphate, lithium sulfate, lithium borate, lithium silicate.

Abstract

The present invention relates to non-aqueous electrolyte secondary batteries. The negative electrode contains, as main a component, composite particles constructed in such a manner that at least part of the surface of nuclear particles comprising at least one of tin, silicon and zinc as a constituent element, is coated with a solid solution or an inter-metallic compound composed of elements included in the nuclear particle and at least one element, exclusive of the element included in said nuclear particle, selected from a group of elements in a Periodic Table, comprising group 2 elements, transition elements, group 12 elements, group 13 elements and group 14 elements exclusive of carbon. The batteries of the present invention include non-aqueous electrolytic solution and solid electrolytes comprising polymer gel electrolytes. The construction of the present invention provides a non-aqueous electrolytic secondary battery with which a possibility of the generation of gas is extremely low when stored at high temperatures. It also provides a battery having higher capacity, and superior cycle properties, high-rate charge/discharge properties.

FIG. 1

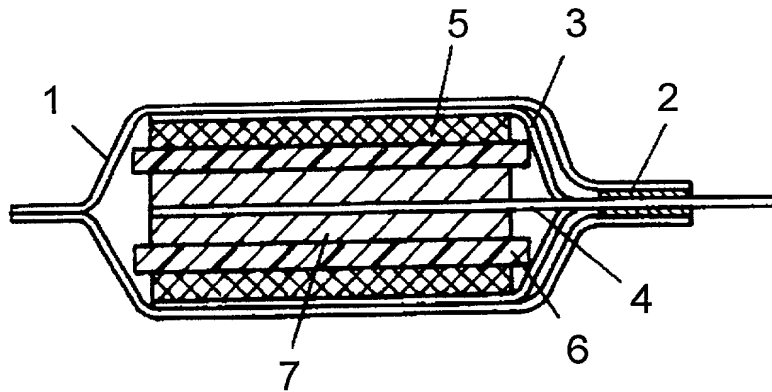
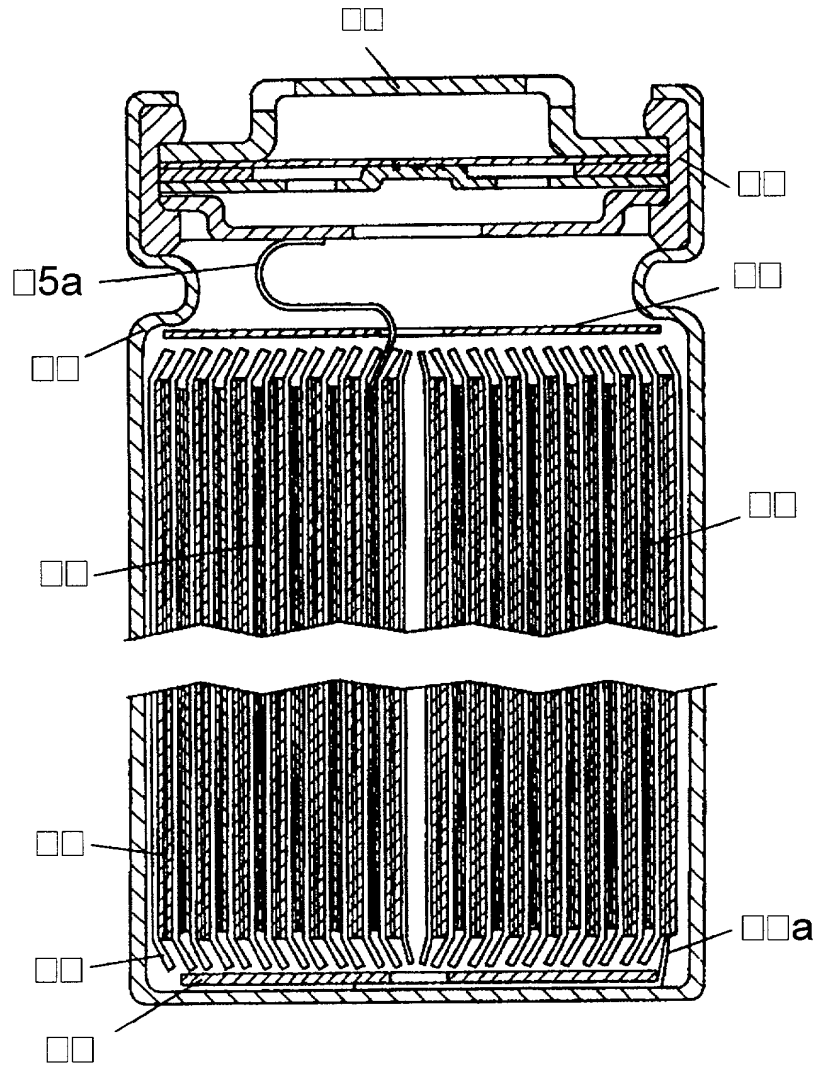


FIG. 2



Reference numerals

- 1 battery casing
- 2 welding seal for lead
- 3 positive electrode lead
- 4 negative electrode lead
- 5 positive electrode plate
- 6 polymer gel electrolyte
- 7 negative electrode
-
- 11 battery casing
- 12 sealing plate
- 13 insulating gasket
- 14 electrode plate group
- 15 positive electrode plate
- 15a positive electrode lead
- 16 negative electrode plate
- 16a negative electrode lead
- 17 solid electrolyte sheet
- 18 Insulating rings

Declaration and Power of Attorney For Patent Application

English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

NON-AQUEOUS ELECTROLYTE SECONDARY BATTERY,

the specification of which is attached hereto unless the following box is checked:



was filed on November 30, 1999 as

United States Application Number or PCT International Application Number PCT/JP99/06686

and was amended on July 31, 2000 (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)

Priority Not Claimed

10-342893

Japan

2 December 1998

(Number)

(Country)

(Day/Month/Year Filed)

☐

10-342894

Japan

2 December 1998

(Number)

(Country)

(Day/Month/Year Filed)

☐

10-342885

Japan

2 December 1998

(Number)

(Country)

(Day/Month/Year Filed)

☐

10-342886

Japan

2 December 1998

(Number)

(Country)

(Day/Month/Year Filed)

☐

I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Number)

(Filing Date)

(Status - patented, pending, abandoned)

(Application Number)

(Filing Date)

(Status - patented, pending, abandoned)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

19 Paul F. Prestia	Reg. No. 23,031	Lawrence E. Ashery	Reg. No. 34,515	Mark J. Marcelli	Reg. No. 36,593
Allan Ratner	Reg. No. 19,717	Christopher R. Lewis	Reg. No. 36,201	Jack J. Jankovitz	Reg. No. 42,690
Andrew L. Ney	Reg. No. 20,300	Robert L. Andersen	Reg. No. 25,771	Jonathan H. Spadt	Reg. No. 45,122
Kenneth N. Nigon	Reg. No. 31,549	Joshua L. Cohen	Reg. No. 38,040	Christopher I. Halliday	Reg. No. 42,621
Kevin R. Casey	Reg. No. 32,117	Daniel N. Calder	Reg. No. 27,424	Scott A. McKeown	Reg. No. 42,866
Benjamin E. Leace	Reg. No. 33,412	Louis W. Beardell, Jr.	Reg. No. 40,506		
James C. Simmons	Reg. No. 24,842	Jacques L. Etkowicz	Reg. No. 41,738		

Address all correspondence to: Lawrence E. Ashery

Ratner & Prestia, Suite 301, One Westlakes, Berwyn, P.O. Box 980, Valley Forge, PA 19482-0980

Address all telephone calls to: Lawrence E. Ashery at (610) 407-0700.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole or first inventor (given name, family name) Kenichi Morigaki

Inventor's signature Kenichi Morigaki Date October 17, 2000

Residence Hyogo, Japan

Citizenship Japanese

Post Office Address 16-40-502, Takagihigashi-cho, Nishinomiya-shi
Hyogo 663-8033 Japan

Full name of second joint inventor, if any (given name, family name) Kazuya Iwamoto

Second Inventor's signature Kazuya Iwamoto Date October 17, 2000

Residence Osaka, Japan

Citizenship Japanese

Post Office Address 2-19-20, Ebaraji-cho, Sakai-shi
Osaka 593-8304 Japan

☒ Additional inventors are being named on separately numbered sheets attached hereto.

30 Full name of third joint inventor, if any (given name, family name) Hizuru Koshina

Third inventor's signature Hizuru Koshina Date October 17, 2000

Residence Osaka, Japan JFX

Citizenship Japanese

Post Office Address 30-2-214, Miiminami-machi, Neyagawa-shi,
Osaka 572-0019

4-00 Full name of fourth joint inventor, if any (given name, family name) Harunari Shimamura

Fourth inventor's signature Harunari Shimamura Date October 17, 2000

Residence Osaka, Japan JFX

Citizenship Japanese

Post Office Address 2-56-3, Kuzuhanoda, Hirakata-shi,
Osaka, 573-1103 Japan

5-00 Full name of fifth joint inventor, if any (given name, family name) Yoshiaki Nitta

Fifth inventor's signature Yoshiaki Nitta Date October 17, 2000

Residence Osaka, Japan JFX

Citizenship Japanese

Post Office Address 1-53-6, Nishifunahashi, Hirakata-shi
Osaka 573-1122 Japan

Full name of sixth joint inventor, if any (given name, family name) _____

Sixth inventor's signature _____ Date _____

Residence _____

Citizenship _____

Post Office Address _____

Full name of seventh joint inventor, if any (given name, family name) _____

Seventh inventor's signature _____ Date _____

Residence _____

Citizenship _____

Post Office Address _____